



# Modeling of synergistic effects in flame inhibition by 2-H heptafluoropropane blended with sodium bicarbonate

V.I. Babushok<sup>a,\*</sup>, K.L. McNesby<sup>b</sup>, A.W. Miziolek<sup>b</sup>, R.R. Skaggs<sup>b</sup>

<sup>a</sup>National Institute of Standards and Technology, Gaithersburg, MD 20899  
<sup>b</sup>U. S. Army Research Laboratory, Aberdeen Proving Ground, Aberdeen, MD 21005

Received 22 May 2002; received in revised form 14 November 2002; accepted 16 December 2002

## 1. Introduction

Environmental concerns related to the destruction of stratospheric ozone has initiated the phasing out of the ubiquitous fire-fighting agent Halon 1301 (CF<sub>3</sub>Br) from the U.S. Army inventory. 2-H heptafluoropropane (C<sub>3</sub>F<sub>7</sub>H, FM-200, HFC-227ea) has been identified as one of the alternative agents for uncoccupied spaces of critical installations formerly protected by Halon 1301. For occupied spaces, where fires must be suppressed in a short period of time (250 ms), to minimize exposure to extreme heat and toxic fumes, a mixture of C<sub>3</sub>F<sub>7</sub>H with sodium bicarbonate (NaHCO<sub>3</sub>) or water with potassium acetate has been chosen as a leading halon replacement candidate [1,2]. Substituting C<sub>3</sub>F<sub>7</sub>H for Halon 1301 typically requires increasing the volumetric suppression concentration relative to Halon [3]. The increased concentration requirement for C<sub>3</sub>F<sub>7</sub>H, while effective, becomes of concern toxicologically because the principal decomposition product of C<sub>3</sub>F<sub>7</sub>H or any hydrofluorocarbon suppressant is hydrogen fluoride (HF). A potential HF mitigation pathway, which has been tested, is the combination (blend) of C<sub>3</sub>F<sub>7</sub>H with sodium bicarbonate (NaHCO<sub>3</sub>). Sodium bicarbonate acts as a HF scavenger with formation of NaF [2]. However, it is well known that sodium-containing compounds also are highly effective flame inhibitors [4–8], and, thus, HF levels might be reduced because the sodium bicarbonate reduces C<sub>3</sub>F<sub>7</sub>H suppression concentrations, hence decreasing HF production.

\*Corresponding author. Tel.: +301-975-5109; fax: +301-975-3672.  
E-mail address: babushok@misl.gov (V. I. Babushok).

## 2. Kinetic model

Even though C<sub>3</sub>F<sub>7</sub>H/NaHCO<sub>3</sub> fire suppressions systems have demonstrated effectiveness under test and evaluation studies [1,2], the flame inhibition mechanism of this halon alternative has not been studied. In this communication, the possible synergistic effect of blending C<sub>3</sub>F<sub>7</sub>H with NaHCO<sub>3</sub> on hydrocarbon flame propagation and HF reduction will be investigated through numerical modeling of inhibited premixed methane/air flames.

The kinetic model for inhibition of methane flame by C<sub>3</sub>F<sub>7</sub>H/NaHCO<sub>3</sub> blend was assembled using several kinetic sub-models. The kinetic model for inhibition by C<sub>3</sub>F<sub>7</sub>H was adopted from the previous work of Williams et al. [9], which is based on the kinetic models of Burgess et al. [10] and Hynes et al. [11]. The kinetic submodel describing the effect of sodium species is based on the works of Zamansky et al. [12] and Williams et al. [13]. Kinetic data for reactions with sodium-containing species were updated using the National Institute of Standards and Technology (NIST) chemical kinetics database [14] along with the addition of new reactions. The reactions with the following sodium species were considered: Na, NaO, NaOH, NaO<sub>2</sub>, Na<sub>2</sub>O, Na<sub>2</sub>O<sub>2</sub>, (NaOH)<sub>2</sub> and NaH. Thermochemical data for sodium-containing species were taken from the work of Gurvich et al. [15,16]. An additional block of reactions to describe formation of NaF and NaF<sub>2</sub> in reactions between sodium- and fluorine-containing species was included as well. Where needed, the kinetic parameters were estimated based on analogous reactions and thermochemistry. The methane/air flame reaction proceeding was mod-

Table 1

Key reactions of sodium containing species ( $k = A T^b \exp(-E/RT)$ , mol, s, cm, cal)

Reaction	A	B	E	Reference
Na + OH + M = NaOH + M				
H <sub>2</sub> /2.0/H <sub>2</sub> O/6.0/ CH <sub>4</sub> /2.0/ CO/1.5/ CO <sub>2</sub> /2.0/	1.82E + 21	−1	0	18, 13
NaO + H = Na + OH	2.0E + 14	0	0	12, 13
NaO + O = Na + O <sub>2</sub>	2.23E + 14	0	0	19, 13
NaO + H <sub>2</sub> O = NaOH + OH	1.3E + 13	0	0	20, 13
NaO <sub>2</sub> + OH = NaOH + O <sub>2</sub>	2.0E + 14	0	0	12, 13
NaOH + H = Na + H <sub>2</sub> O	1.07E + 13	0	1970	18, 13
NaOH + CH <sub>3</sub> = Na + CH <sub>3</sub> OH	1.5E + 13	0	8000	est
Na + O <sub>2</sub> (+M) = NaO <sub>2</sub> (+M)	3.61e + 14	0	0	19, 21
Low / 4.86e21 −1.5 0.0 /				
H <sub>2</sub> /2.0/H <sub>2</sub> O/6.0/ CH <sub>4</sub> /2.0/ CO/1.5/ CO <sub>2</sub> /2.0/				
NaO + H + M = NaOH + M	1.e17	0	0	est
NaO <sub>2</sub> + H = NaOH + O	1.2e11	0.5	0	21
Na + CF <sub>2</sub> O = NaF + CF <sub>2</sub> O	1.4E + 14	0	17000	est
NaF + H = HF + Na	2.0E + 13	0	6500	est

eled using Grimech-3.0 [17]. The overall C<sub>3</sub>F<sub>7</sub>H/NaHCO<sub>3</sub> gas phase kinetic model contains 1075 reactions with 108 species. Table 1 contains kinetic data for key reactions with sodium-containing species.

The decomposition of NaHCO<sub>3</sub> was represented in the kinetic model by the overall chemical processes [7,22]: 1) NaHCO<sub>3</sub>(s) → 0.5Na<sub>2</sub>CO<sub>3</sub>(s) + 0.5H<sub>2</sub>O + 0.5CO<sub>2</sub>, and 2) Na<sub>2</sub>CO<sub>3</sub>(s) → Na<sub>2</sub>O + CO<sub>2</sub>. The decomposition of sodium bicarbonate (melting point 270°C) is an endothermic process ( $\Delta H = 135$  kJ/mol) with formation of highly porous Na<sub>2</sub>CO<sub>3</sub> particles [22]. Above 400°K the decomposition is very fast. The measurements of the overall “bulk” reaction rate demonstrate a first-order dependence based on the amount of unreacted NaHCO<sub>3</sub> ( $A = 1.43E11$ , 1/s;  $E = 102$  kJ/mol; 373–473 K, particle size 125  $\mu$ m) [22]. These data are close to the results of Wu et al. [23] for particles with a diameter of 47  $\mu$ m. Na<sub>2</sub>CO<sub>3</sub> decomposes further to Na<sub>2</sub>O. Na<sub>2</sub>O reacts with water vapor heterogeneously or homogeneously with formation of NaOH [24]. Kinetics of Na<sub>2</sub>CO<sub>3</sub> decomposition was studied by Zamansky et al. [24]. For conditions of their work, decomposition was observed at temperatures below 1000°K. Calculations of equilibrium concentrations demonstrate that the main product above 1200 to 1400°K is sodium hydroxide [24]. In the presence of moisture or in aqueous solution, NaHCO<sub>3</sub> hydrolysis occurs, relatively fast, through the following two overall reactions: 3) NaHCO<sub>3</sub> + H<sub>2</sub>O = NaOH + H<sub>2</sub>CO<sub>3</sub>, and 4) H<sub>2</sub>CO<sub>3</sub> = H<sub>2</sub>O + CO<sub>2</sub>. For modeling purposes, one-step and two-step overall kinetics of decomposition were used. Numerical experiments demonstrate relative insensitivity of results to details of decomposition in agreement with our previous results for DMMP (dimethyl methylphosphonate)

[25] and ferrocene-inhibited flames [26]. Note that the use of this simplified approach to kinetics of sodium bicarbonate decomposition assumes that inhibitor particles completely evaporize in flame zone. Estimates from several works [4,27,28] indicate that for typical hydrocarbon flames (burning velocity ~20–50 cm/s), particles with diameters <20  $\mu$ m will evaporize in the flame reaction zone. Inclusion of overall decomposition kinetics into the kinetic model provides some reasonable delay of inhibitor particle transition to the gas-phase sodium-containing species. Modeling showed that for assumed kinetic data, the replacement of NaHCO<sub>3</sub> by equivalent concentration of gas-phase sodium-containing species leads to approximately the same results.

For the numerical simulations, the Chemkin software package (version 3.6) was used [29]. Comparison of modeling results with available experimental data on flame velocity decreases of methane/air by NaHCO<sub>3</sub> [4] and by C<sub>3</sub>F<sub>7</sub>H [30] demonstrates reasonable agreement.

### 3. Results and discussion

Figure 1 contains dependencies of burning velocities on additive concentration calculated for different NaHCO<sub>3</sub>/C<sub>3</sub>F<sub>7</sub>H blend compositions. The results demonstrate that addition of a relatively small amounts of NaHCO<sub>3</sub> to C<sub>3</sub>F<sub>7</sub>H substantially decreases the amount of C<sub>3</sub>F<sub>7</sub>H required for the same decrease of burning velocity. Note that mixture [C<sub>3</sub>F<sub>7</sub>H]:[NaHCO<sub>3</sub>] = 10:1 (molar ratio) corresponds to currently used agent mixture in many military fire-extinguisher systems [31]. The ratio of suppression concentrations of C<sub>3</sub>F<sub>7</sub>H and NaHCO<sub>3</sub>,

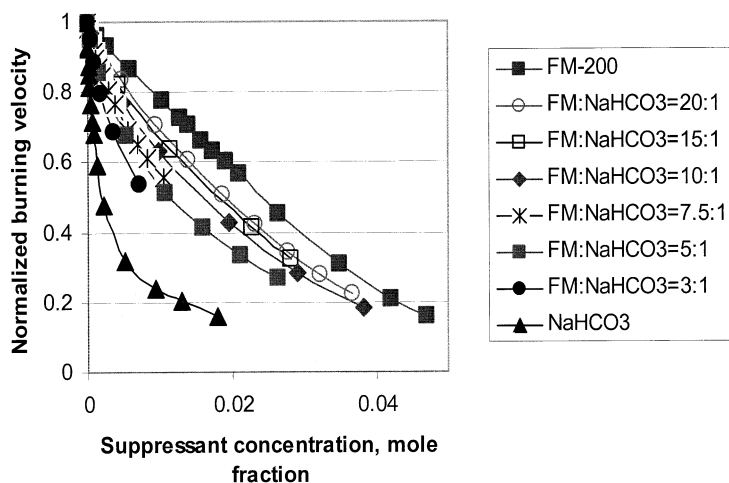


Fig. 1. Dependencies of normalized burning velocity on suppressant concentration for stoichiometric methane/air mixture and different blend compositions (burning velocity of stoichiometric mixture without inhibitor was used for normalization).

when used individually, is approximately 3.2 based on the data of Moore et al. [3] and Hamins [6] (cup burner test, heptane). The ratio of  $C_3F_7H$  and  $NaHCO_3$  concentrations required to decrease the burning velocity by one half for a stoichiometric methane/air mixture (when loaded individually) is approximately 11.7 based on flame calculations. Also presented are the results of calculations for a 10:1 mixture, when the block of reactions describing interaction between sodium- and fluorine-containing species was excluded from the kinetic model (Fig. 2). It shows that the inhibition effect for mixture of agents influencing the radical pool independently is larger. Thus, the synergistic effect of  $C_3F_7H$ /

$NaHCO_3$  blend is negative. Here, synergistic effect is the difference between effects of mixtures of agents acting independently and agents acting with inclusion of chemical interaction between sodium and fluorine subsystems. Note that McDonald et al. [32] discussed synergetic effect as a result of flame temperature change due to suppressant addition.

Figure 3 contains sensitivity coefficients of burning velocity to the rate constants of reactions of sodium- and fluorine-containing species. The presented data correspond to an approximately 40% decrease of burning velocity. It can be seen that the burning velocity decrease is mostly determined by reactions of sodium species

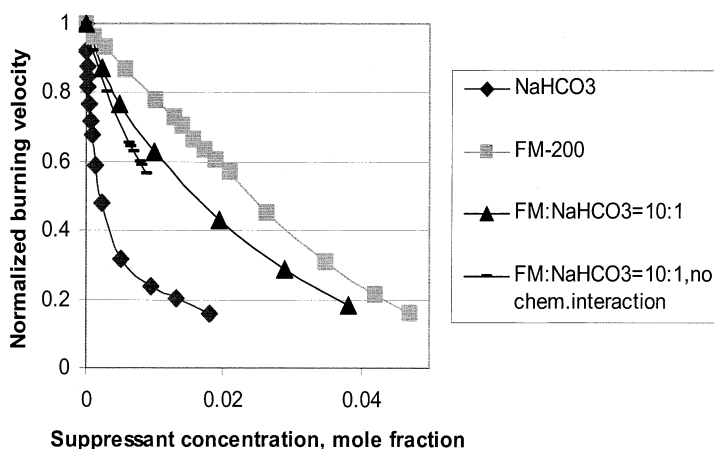


Fig. 2. Dependence of normalized burning velocity on suppressant concentration. Comparison of modeling results with and without reactions describing interaction of fluorine- and sodium-submodels (stoichiometric methane/air mixture, 1 atm).

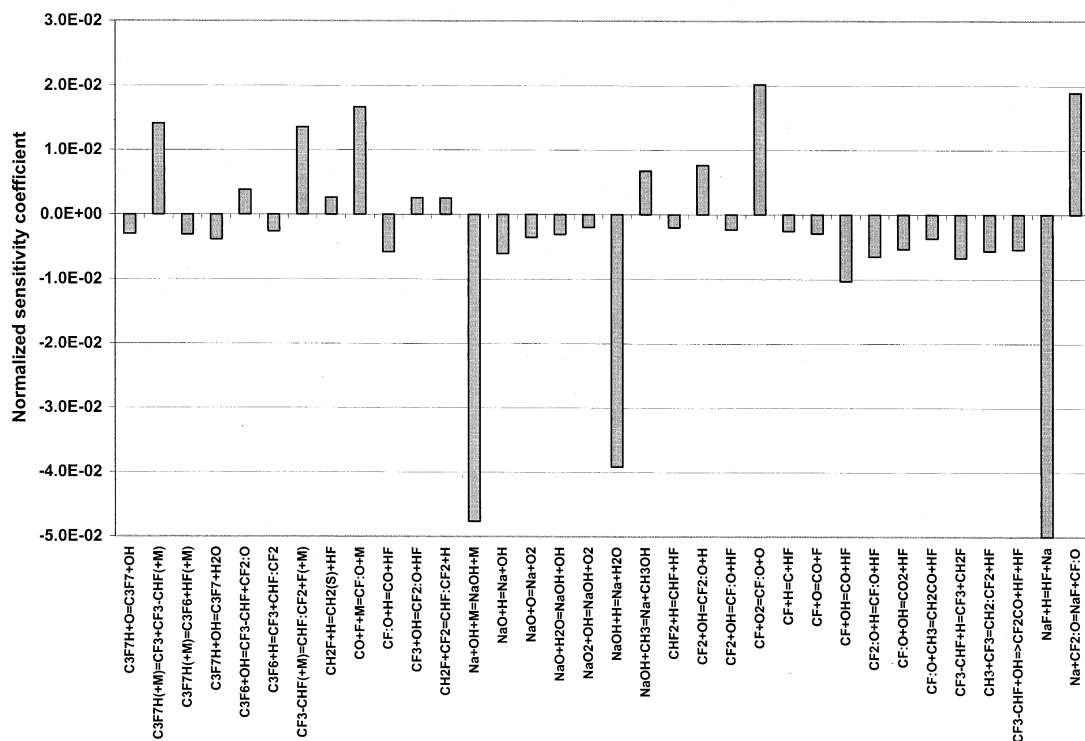
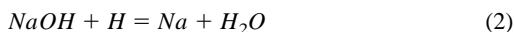
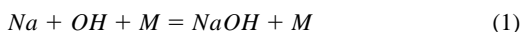


Fig. 3. Burning velocity sensitivity to the rate constants of additive reactions (stoichiometric methane/air mixture; 1% additive,  $C_3F_7H/NaHCO_3 = 10/1$ ; level of presentation is 0.04 of sensitivity coefficient for  $NaF + H = HF + Na$ , which is approximately 10% of sensitivity coefficient for  $H + O_2 = OH + O$  reaction).



Reaction pathway analysis shows that formation of sodium fluoride proceeds in the flame reaction zone mostly through the reaction  $Na + CF_2O = NaF + FCO$ . Decomposition of FCO radical leads to formation of CO and F atoms. Thus, the reaction  $NaF + H = HF + Na$  does not provide termination of chain carriers due to formation of F atoms and the following formation of hydroxyl radical in the reaction  $F + H_2O = HF + OH$ . Actually, formation of NaF decreases the concentration of sodium species available for participation in the catalytical recombination cycle (reactions 1 and 2). Additionally, sodium atoms replace hydrogen atoms in the conversion of  $CF_2O$ . Both of these effects decrease the inhibition effect of  $C_3F_7H/NaHCO_3$  blend to some degree.

Flame equilibrium calculations demonstrate that for mixture compositions  $[C_3F_7H]/[NaHCO_3] > 3$ , the main product containing sodium atom at the equilibrium is NaF. The amount of HF acid scavenged by sodium in the flame reaction zone is relatively small

due to the small  $[Na]/[F]$  ratio. Estimation based on recent experimental data on HF absorption by sodium bicarbonate at room temperature of Mather [33] shows the scavenging efficiency  $\sim 6.6 \times 10^{-4}$  g HF per 1g  $NaHCO_3$  (particle size 7–50  $\mu m$ ; molar efficiency  $\sim 1/400$ ). Note that in real post-fire environment there will be an additional destruction and decomposition of sodium bicarbonate particles released into the protected space, which lead to an additional HF scavenging by sodium-containing species during the cooling and mixing process of combustion products. The advantage of the use of blend of suppressants is the increase of suppression effectiveness while blend provides reasonably good physical properties for its release by fire extinguishers. Thus, decreased HF concentration level during fire suppression by  $C_3F_7H/NaHCO_3$  blend is the result of increased inhibition effectiveness of heptafluoropropane blended by sodium bicarbonate with minor contributions of solid particle-gas phase HF scavenging during mixing of cooled combustion products with the surrounding post-suppression atmosphere that contains fire suppressant after flame extinguishment.

## Acknowledgments

The authors are grateful to B. Williams of the Naval Research Laboratory for providing kinetic models of flame inhibition by  $C_3F_7H$  and sodium-containing compounds and helpful discussions. This work was financially supported through the U.S. Army Research Laboratory mission program on vehicle protection.

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